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Coordination of isocyanide and reduction of cyclooctatetraene by a homoleptic uranium(III) aryloxide, and characterisation of the heteroleptic uranium(III) dimer [{U(N'')$_2$(thf)(μ-I)}$_2$]

Stephen M. Mansell[1,2] and Polly L. Arnold[1]*

[1]*EaStCHEM School of Chemistry, University of Edinburgh, the King's Buildings, Edinburgh, EH9 3FJ, UK; E-Mail: Polly.Arnold@ed.ac.uk*

[2]*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK; E-Mail: S.Mansell@hw.ac.uk*

Abstract

[U(ODtbp)$_3$] (ODtbp = O-2,6-^{t}Bu$_2$C$_6$H$_3$) reacts in a 1:1 ratio with the isocyanide CN-Xyl (Xyl = 2,6-Me$_2$C$_6$H$_3$) to form the *pseudo*-tetrahedral 4-coordinate adduct [U(CNXyl)(ODtbp)$_3$] with ν_{CN} 24 cm^{-1} higher compared to the free isocyanide. Uranium(III) complexes with bulky ligands UX$_3$ (X: ODtbp, N'' = N(SiMe$_3$)$_2$) react with cyclooctatetraene (COT) in a 2:1 U:COT ratio to generate the half-sandwich U^{IV} [U(COT)X$_2$] and [UX$_4$] (which for X = N'' spontaneously converts into the more stable metallacycle [U(N'')$_2${κ^2-N(SiMe$_3$)SiMe$_2$CH$_2$}] and HN''), as opposed to the other potential product, the inverse COT-sandwich [(UX$_2$)$_2$(μ-COT)]. The heteroleptic U^{III} amido-iodide [{U(N'')$_2$(thf)(μ-I)}$_2$] can be isolated in a low yield (14%) from the 2:1 reaction of KN'' and [UI$_3$(thf)$_4$] in thf, and its molecular structure was shown to be dimeric with iodine atoms bridging the U centres.

Keywords

Uranium; amide; aryloxide; cyclooctatetraene; actinide complexes; reduction; f-block organometallics

Introduction

Low-valent uranium chemistry has attracted a lot of interest over the past decade,[1-4] highlighted by the recent characterisation of the U^{2+} oxidation state in molecular compounds.[5, 6] In particular, the ability of molecular U^{3+} compounds to react directly with small molecules such as arenes,[7, 8] dinitrogen[9-15] and CO_2[16] has raised the potential of f-block catalysts which can react with cheap and readily available starting materials using distinctly different reactivity compared to the transition metals.[17]

The interaction of f-block organometallic compounds with CO has a long history with pioneering reactivity demonstrated over 30 years ago for Cp-supported thorium dialkyls and dihydrides.[18] The first f-block complex of CO stable above cryogenic temperatures was reported in 1986.[19] Exposure of green solutions of [U(C$_5$H$_4$SiMe$_3$)$_3$] to CO caused a change of colour to burgundy as one equivalent of CO binds, and IR spectroscopy showed a ν_{CO} band at 1976 cm^{-1}. This band has lowered in frequency significantly upon

coordination (free CO: 2143 cm^{-1}), which is reminiscent of transition metal carbonyl binding, and population of the CO π* orbital with electron density from uranium was proposed.[20] The first crystallographically characterised f-block CO compound, $[U(CO)(C_5Me_4H)_3]$, contained a similar ligand set, and an even lower ν_{CO} band at 1900 cm^{-1} was observed in solution demonstrating a remarkable ligand effect.[21, 22] Subsequently the crystal structure of $[U(CO)(Cp^*)_3]$ was also reported with ν_{CO} at 1922 cm^{-1} ($Cp^* = C_5Me_5$).[23] A theoretical study characterised the back-bonding interaction in $[U(CO)(Cp')_3]$ ($Cp' = Cp, C_5H_4SiMe_3, C_5Me_4H, Cp^*$) as resulting from the transfer of electron density from the Cp′ ligands to the CO.[24] A bridging CO has also been characterised in a mixed-valent $U^{IV/III}$ diuranium system.[25] It is the subsequent reactivity of U carbonyls that has been a particularly important development and one which differentiates 5f reactivity with d-block carbonyl chemistry. A recent report of the conversion of CO and H_2 into a uranium-bound methoxide is a remarkable example of small molecule activation by an f-block complex,[26] and U^{3+} compounds have also demonstrated reductive coupling of two,[14, 27-29] three[30] and four[31] molecules of CO.

Due to the relative scarcity of f-block CO complexes, other ligands have also been used to probe the potential π-donating nature of uranium compounds. Dinitrogen and isocyanides (CN-R) are isoelectronic to CO, and isocyanides are known to function as stronger σ-donors but weaker π-acceptors compared to CO. The uranium isocyanide complex $[U(CNEt)(C_5H_4SiMe_3)_3]$ was originally studied as a proxy for the CO compound which was not crystallised. The energy of the CN stretch, ν_{CN}, of the complex (2160 cm^{-1}) was higher than in free CNEt (2151 cm^{-1}),[32] similar to $[U(CNCy)(Cp)_3]$ (Cy = cyclohexyl) which showed ν_{CN} to be 25cm^{-1} higher than in the free isocyanide.[33]. Both indicated a strengthening of the CN bond and no evidence of π back-donation from the U centre. ~~This was originally~~ In a subsequent in-depth study of many $U(Cp')_3$ derivatives with both alkyl and aryl isocyanides,[21] the authors found that ν_{CN} increased slightly for complexes of the alkyl isocyanides but decreased slightly for the aryl isocyanides giving evidence of U back donation to the isocyanide ligand, particularly when the aryl isocyanide CNXyl (Xyl = 2,6-$Me_2C_6H_3$) was used. The difference in binding between alkyl- and aryl-isocyanides is mirrored in their reactivity as U^{III} complexes of alkyl isocyanides were often found to be unstable with respect to the formation of U^{IV} cyanide compounds.[21] This was also observed in the bond cleavage reaction of CN^{t}Bu with UCp^*_3 which generated the trimeric cyanide complex $[\{U(Cp^*)_2(CN^tBu)(\mu\text{-}CN)\}_3]$ instead of simple coordination.[34] $[U(N'')_3]$ has not been found to coordinate or react with CN^{t}Bu.[19]

Uranium compounds feature large ionic radii and the stability of these compounds depends on the ligand framework. Multi-dentate ligands have often been utilised (such as triamidoamine[35] and the tris-aryloxide substituted triazacyclononane[36]), but the traditional set of non-chelating and kinetically stabilising ligands such as $N(SiMe_3)_2$ (N'') and other bulky amides,[37] alkoxide and aryloxide ligands[38] and Cp derivatives still predominate. The dianion of *cyclo*-octatetraene, $[COT]^{2-}$, is a particularly useful dianionic ligand for the f-block ions due to their large ionic radii, and has a long track record of use as a supporting ligand for uranium.[39] $[U(COT)_2]$ was an instrumental molecule in the history of actinide chemistry and $[COT]^{2-}$ is still widely used as a supporting ligand for small molecule activation.[40] With U^{III}, the ancillary ligand is predominantly Cp* or another derivative,[41] but with U^{IV} the ancillary ligands are much more varied, and examples of piano-stool

complexes with halide,[42, 43] acetylacetonate,[42] BH_4,[44] alkoxide[45] and amide[46, 47] co-ligands are known. COT has also demonstrated binding modes beyond standard half-sandwich complex formation as seen in reactions using a 2:3 ratio of $[U(Cp^*)_3]$:COT; $[\{(Cp^*)(C_8H_8)U\}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_8H_8)]$ formed with an unusual η^3-bridging binding mode.[48] The inverse sandwich-complex $[\{U\{NC(^t Bu)(Mes)\}_3\}_2(\mu\text{-COT})]$, with stabilising ketimide co-ligands, has been synthesised from the reaction of COT with [U{NC(tBu)(Mes)}{NC(tBu)(Mes)(μ-0.5K)}$_2$]$_2$(μ-naphthalene), or from the reaction of [U(COT){NC(tBu)(Mes)}{NC(tBu)(Mes)(μ-0.5K)}$_2$] with [U(I){NC(tBu)(Mes)}$_3$(dme)], demonstrating δ-bonding in the inverse sandwich interaction.[49] Analysis of the bonding situation in 5f complexes of unsaturated carbocycles continues to be an active field of study in order to probe covalency and the degree of different orbital contributions.[50] f-Block complexes of benzene and COT have been found to contain significant δ-interactions,[49-51] but unlike complexes with CO (and isoelectronic species) that can be probed using IR and Raman spectroscopy, direct information about the degree of metal back-bonding in COT complexes is much harder to establish.[52]

The synthesis of $[U(O\text{-}2,6\text{-}^t Bu_2C_6H_3)_3]$, [U(ODtbp)$_3$], was originally reported by Sattelberger and co-workers in 1988,[53] and we have recently studied its reactivity with small molecules, together with the $2,4,6\text{-}^t Bu_3C_6H_2$ derivative, and demonstrated reductive coupling of two molecules of CO, binding of N_2, its reaction with CO_2[14] and the reduction followed by subsequent borylation of arenes (benzene, toluene, biphenyl and naphthalene).[7] Here, we have sought to find the ~~extreme~~ limits to the capability of simple UX_3 systems to reductively couple a π-acceptor such as CO, and to reductively activate ~~π- and~~ δ-acceptors such as benzene. We noted previously that simple coordination of CO was not observed to UX_3, but complexes of [U(ODtbp)$_3$] have been shown to coordinate one or two π-acceptor CN^tBu as ligands.[54] The molecule CNXyl should be a better π-acceptor ligand than CN^tBu, and was considered a good target for this work. We have also explored for UX_3 whether the readily reducible, π-and δ-acceptor *cyclo*-octatetraene (COT) reactivity mimics that of 6- and 10-π arenes which underwent direduction to yield inverse U^{III} arene complexes and $U^{IV}X_4$ by-products. The reaction of COT with [U(N'')$_3$] has briefly been reported,[42] but herein we clarify the reaction products and report the crystal structure of [(COT)U(N'')$_2$].

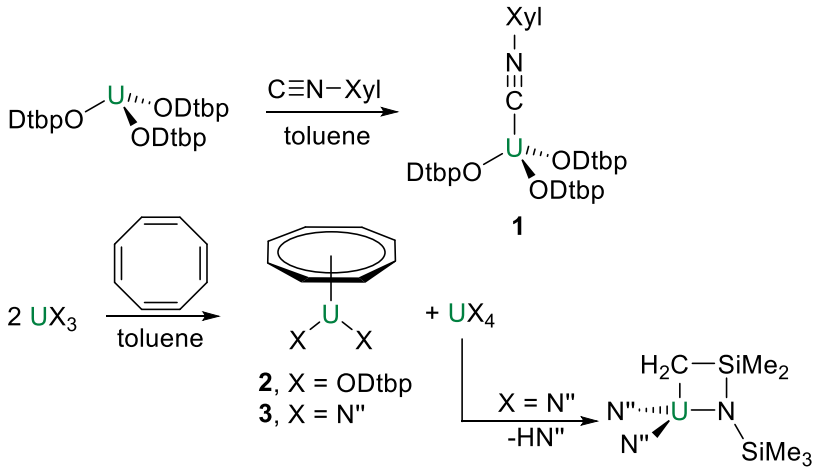
During this work, a by-product from the synthesis of [U(N'')$_3$], a common U^{III} starting material, was discovered which has great potential as a starting material in its own right.

Results and Discussion

Isocyanide coordination

The reaction between [U(ODtbp)$_3$] and one equivalent of CNXyl in toluene immediately produces a dark blue solution, and the isocyanide adduct [U(ODtbp)$_3$(CNXyl)] (**1**) was crystallised from hot *n*-hexane in 54% yield (Scheme 1). ^{1}H NMR spectroscopy reveals sharp resonances assignable to the ODtbp and isocyanide ligands coordinated to a paramagnetic centre. IR spectroscopy as a nujol mull showed the bound isocyanide ν_{CN} at 2138.8 cm^{-1} which is 24 cm^{-1} higher when compared to the free isocyanide (2114.8 cm^{-1}). In previous work, the coordination of one equivalent of CN^tBu to [U(ODtbp)$_3$] showed an increase in ν_{CN} of 43cm^{-1} which is ascribed

to σ-donation of the isocyanide dominating over other interactions.[54] The increase in wavenumber is less for CNXyl, possibly reflecting weaker σ-donation, but this is distinctly different behaviour compared to [U(Cp′)$_3$] complexes of CNXyl. With Cp′ = C_5H_4Me, ν_{CN} was 2060cm^{-1} (a decrease of 54 cm^{-1}), and with Cp′ = C_5Me_4H, ν_{CN} was 2052 cm^{-1} (a decrease of 62 cm^{-1}). In comparison to the Ce analogue [Ce(CNXyl)(C_5H_4Me)$_3$], where σ-donation is expected to dominate, ν_{CN} was found to be 2150cm^{-1}, 36 cm^{-1} higher energy compared to free CNXyl and 90 cm^{-1} higher than that seen for the analogous U complex. These results suggest that [U(ODtbp)$_3$] acts as a weaker π-donor than [U(Cp′)$_3$] derivatives which does not shed any further light on the reasons behind the reactions of [U(ODtbp)$_3$] to reduce N_2 and CO.[14] The complex [U(ODtbp)$_3$(CNXyl)] is thermally stable in C_6D_6 solution at 80 °C overnight and showed no signs of dissociation of the isocyanide ligand; we note that even the poor donor thf cannot be displaced readily from [U(ODtbp)$_3$(thf)].[53]



Scheme 1. Reactions of homoleptic U^{III} compounds with the neutral molecules, xylyl isocyanide and *cyclo*-octatetraene. Xyl = 2,6-$Me_2C_6H_3$, N" = $N(SiMe_3)_2$, ODtbp = O-2,6-$^tBu_2C_6H_3$.

The crystal structure of [U(ODtbp)$_3$(CNXyl)] (Figure 1) showed two molecules in the asymmetric unit with four coordinate, distorted tetrahedral U centres. There are some minor differences in metrics between the two molecules, particularly for the U-CNXyl unit, and combined with some minor twinning, the slightly elongated thermal ellipsoids of the C and N atoms in the isocyanide ligands and the possibility of trace Cl, I or CN impurities co-crystallised in the structure, discussion of the structure will be limited to listing the parameters, and those of the other eight uranium isocyanide complexes listed in the CSD, without drawing any conclusions from the minor differences in bond lengths between U complexes (Table 1). Interestingly, all but one contains Cp′ co-ligands, and as mentioned above, the spectral data of these complexes points to their better π-donor properties than for the [U(ODtbp)$_3$].

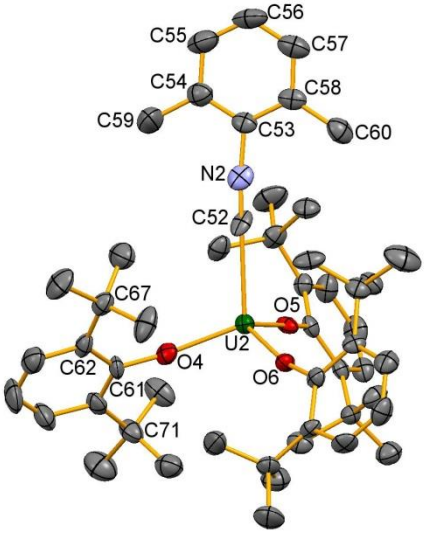


Figure 1. Thermal ellipsoid plot (50% ellipsoid probability) of one of the two molecules of [U(CNXyl)(ODtbp)$_3$] (**1**) present in the asymmetric unit. All hydrogen atoms have been omitted for clarity. Selected bond lengths: U1-O1 2.172(6), U1-O2 2.213(6), U1-O3 2.170(6), U1-C1 2.761(12), N1-C1 1.090(11), U2-O4 2.189(6), U2-O5 2.169(5), U2-C5 2 2.649(10), N2-C52 1.197(12).

Table 1. Selected bond lengths (Å) and angles (°) for structurally characterised uranium isocyanide complexes.

		U-C_{CN}	C=N	U-C-N	C-N-C	Ref.
U^{IV}:	[UCp*$_2$(NMe$_2$)(CN^{t}Bu)$_2$][BPh$_4$]	2.60(1)	1.14(1)	169.7(6)	179(1)	[55]
		2.58(1)	1.16(1)	171.3(6)	178(1)	
	[U{C$_8$H$_6$(Si^{i}Pr$_3$)$_2$}(dimethylpyrazolyl)(CNMe)]	2.675(3)	1.140(3)	170.0(2)	177.3[a]	[56]
	[UCp$_3$(OSO$_2$CF$_3$)(CN^{t}Bu)]	2.59(2)	1.13(2)	175(1)	174[a]	[57]
U^{III}:	[U(C$_5$H$_4$SiMe$_3$)$_3$(CNEt)][b]	2.57(2)	1.16[a]	173.6(2.0)	170.2(2.6)	[20]
	[U(C$_5$Me$_4$H)$_3$(CNC$_6$H$_4$OMe)]	2.464(4)	1.166(6)	173.7(9)	173.5[a]	[21]
	[{UCp*$_2$(CN^{t}Bu)(μ-CN)}$_3$][c]	2.61(5)	1.164(3)	176.5(5)	177.9[a]	[34]
	[U{C$_5$H$_3$(SiMe$_3$)$_2$}$_2$Br(CNtBu)$_2$][a]	2.662(8)	1.128	177.1	173.1	[58]
		2.697(7)	1.126	178.4	176.1	
	[U{C$_5$H$_3$(SiMe$_3$)$_2$}$_2$Cl(CN-2,6-Me$_2$C$_6$H$_3$)$_2$][a]	2.654(9)	1.164	168.1	171.1	[59]
		2.681(9)	1.144	171.1	177.5	
	[U(ODtbp)$_3$(CN-2,6,-Me$_2$C$_6$H$_3$)][d]	2.76(1)	1.09(1)	173(1)	176(1)	This work
		2.65(1)	1.20(1)	175(1)	175(1)	

[a] Only some E.S.D.s were available,[b] Four molecules in the asymmetric unit,[c] Av. of three CN^{t}Bu ligands,[d] Two molecules in the asymmetric unit

Reactions with cyclooctatetraene (COT)

Previously, we showed how reactions between homoleptic U^{III} amides and aryloxides with arenes have demonstrated the formation of one equivalent of inverse arene sandwich complex [(μ-arene)(UX$_2$)$_2$] together

with two equivalents of a U^{IV} by-product which provided the two electrons to direduce the arene and maintained the +3 oxidation state of the two bound U centres.[7] Reactions with [U(ODtbp)$_3$] and COT were carried out in toluene to see if an inverse COT sandwich complex could be formed directly, Scheme 1. ^{1}H NMR spectroscopy of the reaction mixture shows resonances for the U^{IV} compound [U(ODtbp)$_4$] together with a singlet resonance for COT bound to a paramagnetic U centre at -35.3 ppm. Integration of the resonances associated with the other ligands in this complex revealed a ratio of two ODtbp ligands to one COT ligand ruling out the formation of the inverse sandwich [{U(ODtbp)$_2$}$_2$(μ-COT)]. Extraction of the product into *n*-hexane and filtration removed the [U(ODtbp)$_4$] by-product and crystallisation of the filtrate yielded pure [U(COT)(ODtbp)$_2$] (**2**) as orange crystalline material. Although crystals suitable for X-ray crystallography have not been grown, the NMR data, together with elemental analysis data, support the formulation of the complex as [U(COT)(ODtbp)$_2$]. In seeking structural data for [U(COT)X$_2$] complexes, the analogous reaction with [U(N")$_3$] was carried out to see if [U(COT)(N")$_2$] could be crystallised instead. This compound is known and was synthesised from [U(COT)Cl$_2$(thf)$_2$] and NaN" in 76% yield,[46] but we were also interested in re-visiting a report detailing the reaction of [U(N")$_3$] with COT which stated that a COT-bound U^{IV} compound was observed by ^{1}H NMR, without any additional details.[42]

The reaction of [U(N")$_3$] with COT can be monitored by paramagnetic ^{1}H NMR spectroscopy which revealed resonances that match those of [U(COT)(N")$_2$] together with resonances for the U^{IV} metallacycle [U(N")$_2${κ^2-N(SiMe$_3$)SiMe$_2$CH$_2$}] and HN" arising from the well-known decomposition of [U(N")$_4$].[7] The reaction therefore proceeds as for [U(ODtbp)$_3$], i.e. generating one equivalent of U^{IV} by-product for every equivalent of [U(COT)X$_2$] formed. Crystals of [U(COT)(N")$_2$] (**3**) suitable for X-ray crystallography were grown from *n*-hexane, and as the structure has not been described before, it is included here. The U centre is bound symmetrically to the COT ligand with two N" ligands making up the rest of the U coordination sphere. The U-C distances (2.668(3) – 2.700(2) Å) are similar to previous U^{IV} examples, such as [U{C$_8$H$_6$(Si^{i}Pr$_3$)$_2$}(dimethylpyrazolyl)(CNMe)],[56] and the U-N distances (2.285(2) and 2.270(2) Å) are similar to those seen in [U{N(SiHMe$_2$)$_2$}$_4$] (2.280(4) and 2.281(4) Å).[60] It is isostructural to the Th analogue, although described in *P*2$_1$/*a* in the original paper, with the Th-N (2.32(1) and 2.35(1) Å) and Th-C distances (2.71(2) – 2.79(2) Å) found to be slightly longer.[46] Potential agostic interactions between Th and two of the carbon atoms in the amide groups were identified in the original publication with distances of 3.147(15) and 3.041(13) Å,[46] and the structure of **3** showed similar contacts at 3.053 and 3.141 Å. A recent experimental and theoretical study by us showed the effects of pressure on U…C distances to the N" groups in [{U(N")$_2$}$_2$(μ-arene)] which demonstrated no agostic interaction at ambient pressure (U…C: 3.025(3) and 3.022(3) Å). Evidence for an agostic interaction was found and characterised at increased pressure (3.2 GPa, U…C: 3.00(5) and 2.95(2) Å) using QTAIM (quantum theory of atoms-in-molecules) computational analysis.[61] Without structural information on both **2** and **3**, we were unable to investigate the influence of these two monodentate ligands on the U-COT bonding situation, although it was anticipated that structural data alone was unlikely to offer substantial evidence.

Decisively, however, neither supporting ligand enabled the formation of a bridged species from simple UX_3 starting materials.

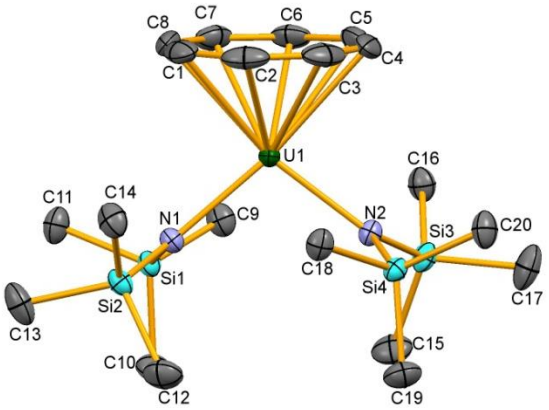
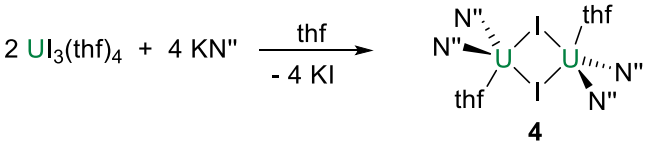


Figure 2. Thermal ellipsoid plot (50% ellipsoid probability) of [U(COT)(N")$_2$] (**3**); All hydrogen atoms have been omitted for clarity.

Formation of [{U(N")$_2$(thf)(μ-I)}$_2$] (4)



(2)

During a synthesis of [U(N")$_3$] using [UI$_3$(thf)$_4$] and 2.9 equivalents of KN" in an attempt to suppress all formation of the metallacycle [U(N")$_2${κ^2-N(SiMe$_3$)SiMe$_2$CH$_2$}], a small quantity of dark black, block-shaped crystals were observed, in addition to the typical formation of purple needles of [U(N")$_3$], grown from a concentrated *n*-hexane solution placed at -25°C for 16 hours. X-ray crystallographic analysis revealed the compound to be [{U(N")$_2$(thf)(μ-I)}$_2$] (**4**) which contained two U^{III} centres bridged by two iodine atoms and further ligated by two N" ligands and a molecule of thf (Figure 3). Rational syntheses following equation 2, using two equivalents of KN" show the reaction to be repeatable, but the desired product is only made pure in poor isolated yields (14%) as a consequence of the crystallisation required to purify the compound from other by-products.

^{1}H NMR spectroscopy in C_6D_6 revealed a moderately broad signal at -8.88 ppm due to the paramagnetic nature of the U^{III} centres, along with two broad resonances for the thf molecules at -3.71 and -4.25 ppm. Using the Evans NMR method, the magnetic moment was calculated to be 4.8 μ_B, which makes the value of 2.4 μ_B per U centre approximately in the middle of values recorded for bimetallic U^{III} complexes,[62] and lower than the value recorded for monomeric [U{κ^2-{N(Dipp)C(Me)}$_2$C}(N")(I)] (3.1 μ_B).[63]

In the crystal structure, a molecule of [{U(N")$_2$(thf)(μ-I)}$_2$] (Figure 3) is situated over an inversion centre and features approximately equal U-I distances of 3.2121(3) and 3.2562(3) Å and U-N distances of 2.319(3) and 2.309(3) Å, which are similar to those seen in the homoleptic U^{III} amides [U(N")$_3$] (2.320(4) Å)[64] and

[U{N(SiPhMe$_2$)$_2$}$_3$] (2.337(15) Å).[60] The U…U separation is long at 5.006 Å and the U-thf distance (2.542(3) Å) is very close to the mean U-thf distance as determined by a search of the CSD (2.497 Å). The related heteroleptic U^{III} iodide [U{κ^2-{N(Dipp)C(Me)}$_2$C}(N")(I)] has a monomeric structure presumably due to the extra stabilisation of the sterically bulky κ^2-diketiminate ligand, as are [U(L)$_2$I] where L are dihydrobis(pyrazolyl)borate derivatives.[65] Related La^{III} compounds are known, although somewhat surprisingly, given that U^{III} and La^{III} are almost the same size, [{La(N")$_2$(thf)(μ-I)}$_2$] is not isostructural.[66] The related [La{N(SiMe$_3$)(Si^{t}BuMe$_2$)}$_2$(μ-I)]$_2$ which did not feature thf coordination was only characterized by X-ray crystallography.[67]

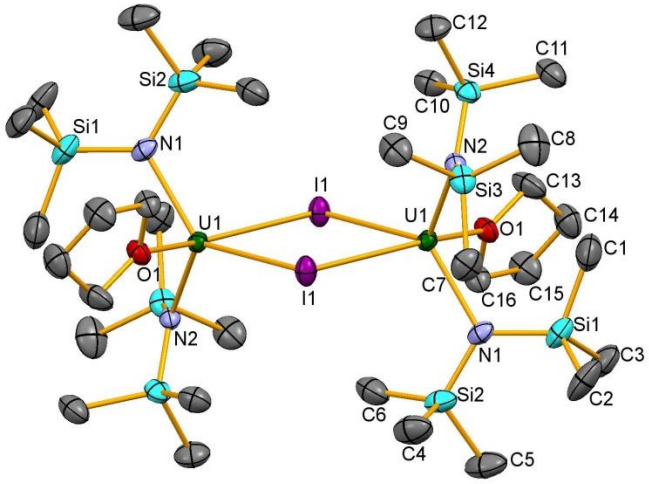


Figure 3. Thermal ellipsoid plot of [{U(N")$_2$(thf)(μ-I)}$_2$] (**4**) (symmetry operator for symmetry generated atoms: -x+1, -y+1, -z+1). All hydrogen atoms have been omitted for clarity.

Conclusions

In the coordination of the isocyanide CNXyl to a homoleptic U^{III} aryloxide σ-donation effects dominate over π-acceptance according to FTIR spectroscopy. Reactions of both homoleptic U^{III} aryloxides and amides tested with COT result in direduction of COT to the [COT]$^{2-}$ dianion and redistribution of the monoanionic ligands, forming the half sandwich complexes [U(COT)X$_2$] (a known molecule for the amide) together with an equivalent of U^{IV} by-product; [U(ODtbp)$_4$] or [U(N")$_4$], the latter of which is not observed directly as it decomposed to the metallacycle [U(N")$_2${κ^2-N(SiMe$_3$)SiMe$_2$CH$_2$}] and HN(SiMe$_3$)$_2$ under the reaction conditions. This reactivity contrasts that observed previously with aromatic arenes, such as benzene and toluene, where inverse sandwich-complexes were formed in a 4:1 U:arene stoichiometry in arene solvent. The isolation of the dimeric U^{III} complex [{U(N")$_2$(thf)(μ-I)}$_2$] in low yield from 2:1 KN":[UI$_3$(thf)$_4$] is hampered by the isolation, but could potentially be a useful starting material in its own right.

Experimental

General details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in MBraun Unilab or Vacuum Atmospheres OMNI-lab gloveboxes unless otherwise stated. Tetrahydrofuran (thf) and *n*-hexane were degassed and purified by passage through activated alumina towers prior to use. All deuterated solvents were boiled over potassium, vacuum transferred, and freeze-pump-thaw degassed three times prior to use. The compounds KN" (from KH and HN" in toluene), CN(2,6-$Me_2C_6H_3$),[68] $[UI_3(thf)_4]$ (from stirring $[UI_3]$[69] in thf), $[U(N")_3]$[70] and $[U(ODtbp)_3]$[14] were made as previously described in the literature, whilst all other reagents were used as purchased without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker AVA 400 or 600 MHz NMR spectrometers at 298 K. Chemical shifts are reported in parts per million, and referenced to residual proton resonances calibrated against external TMS. Infrared spectra were recorded on Jasco 410 spectrophotometers. Solutions for UV-vis spectrophotometry were made in a nitrogen filled glovebox and spectra were recorded in either a Teflon-tapped 10 mm quartz cell or a 1 mm quartz cell sealed by a tight fitting Subaseal on a Unicam UV1 spectrophotometer.

Synthesis of $[U(ODtbp)_3(CN\text{-}2,6\text{-}Me_2C_6H_3)]$ (1)

To a solution of $[U(ODtbp)_3]$ (345 mg, 0.404 mmol) in toluene (5 cm^3) was added a toluene solution of CN(2,6-$Me_2C_6H_3$**)** (53 mg, 0.404 mmol in 1 cm^3) forming a dark blue solution instantaneously. The solution was stirred for 16 hours then all the volatiles were removed under reduced pressure and the product was dissolved in hot *n*-hexane (30 cm^3) which crystallised as dark blue crystals upon cooling to room temperature (166 mg). The supernatant solution was placed at -30 °C to obtain a second crop of crystals (combined yield: 216 mg, 0.219 mmol, 54%).

^1H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 15.75 (d, $^2J_{HH}$ = 8.0 Hz, 6 H, *m*-Dtbp-*H*), 12.77 (t, $^2J_{HH}$ = 8.0 Hz, 3 H, *p*-Dtbp-*H*), 7.55 (br. s, 1 H, *p*-Xyl-*H*), -1.83 (s, 2 H, *m*-Xyl-*H*), -2.45 (s, 54 H, ^{t}Bu), -14.55 (s, 6 H, *o*-Xyl-C*H*$_3$). IR (nujol mull) cm^{-1}: 2138.8 (C=N). UV-vis-NIR (1.14 x 10^{-3} M *n*-hexane solution) λ, nm (ε, M^{-1} cm^{-1}): 655 (867), 773 (494), 1044 (353), 1197 (164), 1219 (172), 1397 (144), 1415 (138). Analysis calculated for $C_{51}H_{72}NO_3U_2$: C, 62.18; H, 7.37; N, 1.42. Found: C, 61.89; H, 7.20; N, 1.38.

Synthesis of $[U(COT)(ODtbp)_2]$ (2)

To a solution of $[U(ODtbp)_3]$ (335 mg, 0.392 mmol, 1.63 equiv.) in toluene (4 cm^3) was added cyclooctatetraene (25 mg, 0.24 mmol, 1 equiv.) in toluene (1 cm^3) forming an orange solution. After 1 hour, this was left to settle and the orange supernatant solution was transferred by filter cannula to a new Schlenk vessel and all the volatiles were removed under reduced pressure. The product was extracted into *n*-hexane (20 cm^3) with vigorous stirring,

then reduced in volume to ca. 2 cm^3 and the mixture was left to settle as the $U(ODtbp)_4$ by-product is not soluble under these conditions. The orange supernatant solution was transferred by cannula filter into a new Schlenk vessel where upon it crystallised at room temperature (66 mg, 0.088 mmol, 45 %).

^1H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 15.10 (d $^3J_{HH}$ = 8.3 Hz, 4 H, *m*-Dtbp-*H*), 11.29 (t $^3J_{HH}$ = 8.3 Hz, 2 H, *p*-Dtbp-*H*), -9.77 (s, 36 H, ^{t}Bu), -35.33 (s, 8 H, COT). Analysis calculated for $C_{36}H_{50}O_2U$: C, 57.44; H, 6.69. Found: C, 57.47; H, 6.75. μ_{eff} (Evans' NMR method) 2.83 μ_B.

Synthesis of [U(COT)(N")$_2$] (3)

A solution of COT (27 mg, 0.26 mmol, 1 equiv.) in toluene (3 cm^3) was added to $[U(N")_3]$ (304 mg, 0.42 mmol, 1.6 equiv.) and the reaction was stirred overnight. All of the volatiles were removed under reduced pressure and the resulting solid was transferred into a sublimation apparatus and the metallacyclic by-product was sublimed at 100°C, 1 x 10^{-6} mbar leaving $[U(COT)(N")_2]$ (53 mg, 0.080 mmol, 38 %). The product was recrystallised from *n*-hexane yielding orange crystals suitable for X-ray diffraction.

^1H NMR data (-33.7 ppm, COT, and -11.1 ppm, N") match literature values.[46]

Synthesis of [{U(N")$_2$(thf)(μ-I)}$_2$] (4)

To a solution of $[UI_3(thf)_4]$ (2.648 g, 2.919 mmol, 1 equiv.) in thf (20 cm^3) was added KN" (1.1645 g, 5.84 mmol, 2 equiv.) in thf (20 cm^3) and the dark purple/black solution was stirred for 16 hours. The solution was left to settle then filtered and the volatiles were removed under reduced pressure. The dark residue was extracted into *n*-hexane (50 cm^3) and transferred by filter cannula into a new Schlenk vessel and stored at -30 °C overnight. Dark black crystals were observed and these were isolated by filter cannula and dried under vacuum (325 mg, 0.208 mmol, 14 %).

^1H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) -3.71 (br. s, 4 H, thf), -4.25 (br. s, 4 H, thf), -8.88 (br. s, 36 H, N"). μ_{eff} (Evans' NMR method) 4.83 μ_B per molecule.

Despite repeated attempts, a satisfactory elemental analysis could not be obtained. This has been observed before for low valent uranium compounds containing silylamides.[60, 71]

Crystallographic details

Crystals suitable for X-ray diffraction analysis were grown from saturated *n*-hexane solutions, mounted in inert oil and then transferred to the cold gas stream of the diffractometer. Diffraction experiments were carried out on an Oxford diffraction Excalibur four-circle diffractometer employing Mo-Kα radiation (λ = 0.71073 Å). The

structures were solved by direct or Patterson methods and refined by least squares on weighted F^2 values for all reflections.[72] All hydrogen atoms were constrained to idealised geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 1. The structure of [**U(ODtbp)$_3$(CN-2,6-Me$_2$C$_6$H$_3$)]** was refined as a 2-component inversion twin with the twin law [1 0 0 0 -1 0 0 0 -1]. One component refined to a small fraction - 0.032(4) - with the others refining approximately to zero.

Table 2. Crystal data and structure refinement details

Identification code	**1**	**3**	**4**
Empirical formula	$C_{54}H_{79}NO_3U$	$C_{20}H_{44}N_2Si_4U$	$C_{32}H_{88}I_2N_4O_2Si_8U_2$
Formula weight	1028.21	662.96	1515.64
Temperature/K	170.15	170.15	170.15
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1/c$	*Pbca*
a/Å	11.1182(2)	17.8873(2)	18.5264(3)
b/Å	20.3955(5)	13.0193(1)	16.3899(2)
c/Å	22.5361(5)	11.9118(1)	19.1118(3)
α/°	90	90	90
β/°	90.4202(17)	90.964(1)	90
γ/°	90	90	90
Volume/Å^3	5110.17(19)	2773.63(4)	5803.22(15)
Z	4	4	4
ρ_{calc}g/cm^3	1.336	1.588	1.735
μ/mm^{-1}	3.216	6.033	6.831
F(000)	2104.0	1304.0	2904.0
Crystal size/mm^3	0.45 × 0.08 × 0.05	0.49 × 0.26 × 0.20	0.15 × 0.12× 0.09
2Θ range for data collection/°	5.706 to 54.994	6.258 to 54.97	5.838 to 54.968
Index ranges	$-14 \le h \le 13$, $-26 \le k \le 26$, $-29 \le l \le 29$	$-23 \le h \le 23$, $-16 \le k \le 16$, $-15 \le l \le 15$	$-24 \le h \le 24$, $-21 \le k \le 21$, $-24 \le l \le 24$
Reflections collected	48945	78463	57615
Independent reflections	22113 [R_{int} = 0.0600, R_{sigma} = 0.1017]	6347 [R_{int} = 0.0318, R_{sigma} = 0.0138]	6650 [R_{int} = 0.0690, R_{sigma} = 0.0407]
Data/restraints/parameters	22113/1/1106	6347/0/256	6650/0/238
Goodness-of-fit on F^2	1.038	1.129	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.0696	R_1 = 0.0162, wR_2 = 0.0371	R_1 = 0.0317, wR_2 = 0.0495
Largest diff. peak/hole / e Å^{-3}	1.87/-1.41	0.57/-0.71	0.75/-0.52

Appendix A. Supplementary data

CCDC 1446017, 1432001 and 1432002 contains the supplementary crystallographic data for **1**, **3** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article (NMR spectra for compounds **1** – **4**, and the UV-vis spectrum of **1**) can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.xxxx.xx.xxx.

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